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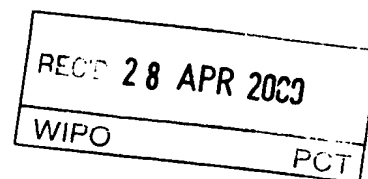
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USE OF A QUATERNARY AMMONIUM GLYCOSIDE SURFACTANT AS AN
ADJUVANT FOR FERTILISERS OR PESTICIDES

The present invention relates to the use of a quaternary ammonium glycoside surfactant as an adjuvant for fertilisers or pesticides, such as herbicides. The surfactants are obtained from ethoxylated quaternary ammonium compounds and reducing saccharides or alkyl glycosides, and the cationic part of the molecule is connected to the sugar residue by a glycosidic bond.

It is well known that both the uptake and efficacy of many fertilisers and pesticides can be improved by the addition of other compounds, adjuvants, and many surfactants have been used for this purpose. The mechanism for their action is complex, and the effect is not only caused by an improved wetting of the leaf surface.

Also the addition of ammonium sulphate to pesticides may improve their efficacy. Many of these formulations are not shelf stable, and must be prepared in place by tank-mixing the pesticide with the ammonium sulphate. However, the addition of surfactants may also be of help in these instances, and compositions containing both a pesticide and ammonium sulphate can acquire an improved stability by the presence of certain surfactants.

It is also an advantage if the adjuvants do not generate a lot of foam when formulations containing pesticides or fertilisers are produced, or when they are applied by spraying.

The most widely used surfactant in commercial formulations containing the well-known herbicide glyphosate is an ethoxylated fatty amine. Many more kinds of surfactants have been used as adjuvants for pesticides, and among them

quaternary ammonium salts have been described. For example in US 5 317 003 and EP-B1-0 274 369 herbicidal compositions containing glyphosate and quaternary ammonium salts are claimed. In US 5 317 003 a herbicidal composition comprising
5 glyphosate salts and an ethoxylated/propoxylated quaternary ammonium surfactant is described, where the weight ratio of surfactant to glyphosate is between about 1:5 to 5:1. This composition is claimed to be non-irritant to the eyes, of low toxicity to aquatic life, and of similar efficacy as the best
10 commercial glyphosate formulations. The solutions are also claimed to be clear and stable. In EP-B1-0 274 369 the compositions also contain ammonium sulphate. In this case the quaternary ammonium salt makes a longer shelf life possible for these herbicidal compositions. However, both the amine
15 ethoxylates and the quaternary ammonium surfactants suffer from the drawback that they are not readily biodegradable.

Surfactants containing sugar residues and nonionic, anionic or cationic groups are known by the publication JP 93-043403. These surfactants are used in pesticide
20 formulations. The ionic part of the molecules described in JP 93-043403 is connected to the sugar residue by an ether bond, which originates from a nonglycosidic hydroxyl substituent on the sugar. This means that the ionic group is not a part of the glycosidic group that contains a large hydrocarbon
25 residue.

In JP 4-193891 cationic sugar surfactants where the cationic part is connected to the sugar residue by a glycosidic bond are described for use as surfactants.

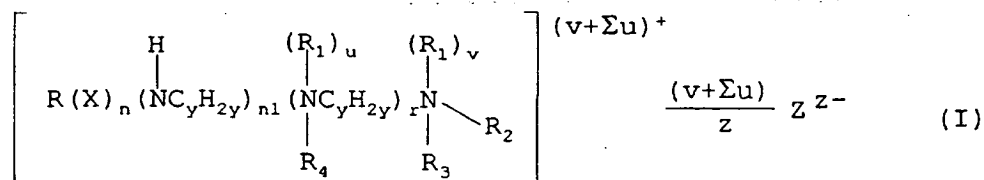
The PCT/SE98/01433 (not yet published) discloses the use
30 of quaternary ammonium glycosides of the same type as in JP 4-193891 as hydrotropes for surfactants.

The purpose of the present invention is to provide adjuvants for pesticide formulations and for formulations containing fertilisers, that are more effective than conventional quaternary ammonium surfactants.

Another purpose is to provide adjuvants with an improved biodegradability compared to prior known quaternary ammonium compounds used as adjuvants.

These purposes can be achieved by using a quaternary ammonium glycoside surfactant containing at least one hydrocarbon group with 6-24 carbon atoms and at least one quaternary ammonium group where at least one substituent is an alkyleneoxy containing group which is connected to a saccharide residue by a glycosidic bond. Preferably the substituent has the formula $(AO)_s(G)_p$ where AO is an alkyleneoxy group with 2-4 carbon atoms, G is a saccharide residue, p is a number from 1 to 10 and s is a number from 1 to 15. These quaternary ammonium glycoside surfactants differ from the above-mentioned ethoxylated quaternary ammonium surfactants in that a greater portion of the alkoxyated part of the molecule is exchanged for sugar residues. The quaternary ammonium glycoside surfactants are disclosed as such in the above-mentioned documents JP 4-193891 and PCT/SE98/01433.

Suitable quaternary ammonium glycoside surfactants according to the invention have the formula

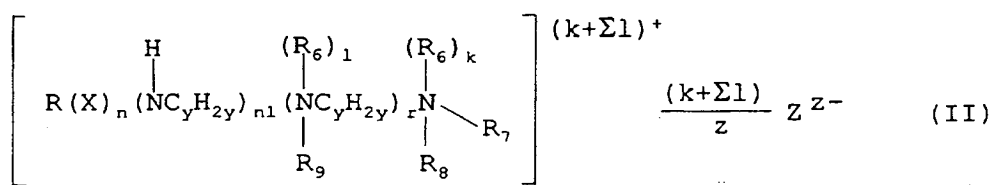


where R is an aliphatic group with 6-24, preferably 8-20 carbon atoms; R_1 is an aliphatic group with 1-4 carbon atoms or $(AO)_s(G)_p$; R_2 , R_3 and R_4 are a group $(AO)_s(G)_p$, an aliphatic group with 1-24 carbon atoms or a hydroxyalkyl group with 2-4 carbon atoms; AO is an alkyleneoxy group with 2-4 carbon atoms; s is 0-15, preferably 1-6 and $\Sigma s = 1-30$, preferably 3-15; G is a saccharide residue which is connected to the rest of the molecule by a glycosidic bond and p (the degree of polymerisation) is 0-10 and $\Sigma p = 1-20$; r = 0-3; y = 2-3; X = CO or $COO(AO)_t(C_qH_{2q})$ or $O(AO)_t(C_qH_{2q})$; n = 0 or 1; n_1 is 0 except when X is CO, then n_1 is 1; q = 2-4; t = 0-4; u = 0 or 1 and v = 0 or 1, provided that the sum $(v + \Sigma u)$ is 1-3, preferably 1; Z is an anion, preferably a monovalent anion, such as Cl^- or methyl sulphate and z is the charge of the anion Z. The nitrogen atoms where u or v is 1 are quaternary and thus have a permanent positive charge. These quaternary ammonium glycoside surfactants have, in comparison with prior known quaternary ammonium surfactants that have been used as adjuvants, an essentially improved biodegradability. When using the quaternary ammonium glycoside surfactants in formulations containing pesticides, such as herbicides, for example glyphosate, the activity of the herbicide is enhanced more than when using the corresponding quaternary ammonium surfactants in the formulations, when comparing activity related to the molar amount of quaternary nitrogen present in the formulations. Also shelf stable formulations containing ammonium sulphate can be obtained when using the quaternary ammonium glycoside surfactants as adjuvants, and these formulations exhibit still larger herbicidal effects. Another advantage when using these glycosides in herbicidal formulations is that highly concentrated formulations can be obtained. At high concentrations of herbicides most other

adjuvants either cause gelling or give rise to highly viscous formulations, whereas formulations containing the quaternary ammonium glycosides remain clear and of a low viscosity. For instance, a formulation in water containing 40.7% a.e. of glyphosate and 8.3% by weight of 3-aminopropyl C₈-C₁₀-alkyl ether + 5 EO that has been quaternised and glucosidised was totally clear and of low viscosity. This makes it easy to dilute the solution to the desired concentration just before use. An additional benefit of these compounds is their foaming behaviour. Many of the quaternary ammonium glycosides according to the present invention are rather low-foaming compounds, and the foam they are generating collapses quickly.

In formulations containing the quaternary ammonium glycosides the amount of glycoside can vary within wide limits, but is normally from 10% to 500% by weight calculated on the amount of pesticide or fertiliser present in the formulation, preferably between 20% to 200%.

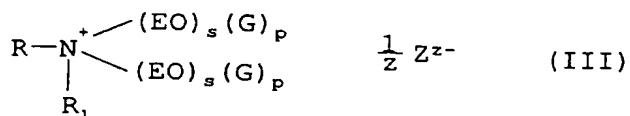
The product (I) can be produced by reacting a) a reducing saccharide or an alkyl glycoside and b) a quaternary ammonium compound having the formula



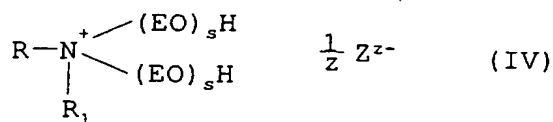
where R₆ is independently an aliphatic group with 1-4 carbon atoms or -CH₂CH₂OH; R₇, R₈ and R₉ independently are a group (AO)_s, an aliphatic group with 1-24 carbon atoms or a hydroxyalkyl group with 2-4 carbon atoms; l = 0 or 1 and k = 0 or

1, provided that the sum $(k + \sum l)$ is 1-3, preferably 1; and R, AO, s, X, n, n_1 , y and r have the same meaning as in formula I. The nitrogen atoms where k or l is 1 are quaternary and thus have a permanent positive charge. The obtained reaction mixture contains essential amounts of both the quaternary ammonium glycoside surfactant I and the quaternary ammonium compound II. This product mixture can advantageously be used without any purification as an adjuvant. Normally the ratio between the quaternary ammonium glycoside surfactant I and the quaternary ammonium compound II is from 1:3 to 9:1.

Suitable examples of the quaternary ammonium glycoside surfactants and the quaternary ammonium compounds are those having the formulae



where R is an aliphatic group with 6-24, preferably 8-20 carbon atoms; R_1 is an aliphatic group with 1-4 carbon atoms or the group $\text{C}_2\text{H}_4\text{O}(\text{G})_p$; G is a saccharide residue that is connected to the polyethyleneoxy chain by a glycosidic bond and p (the degree of polymerisation) is 0-10, preferably 0-5, $\sum p$ being 1-15, preferably 1-8; EO is an ethyleneoxy group; s is 0-12; $\sum s$ is 2-15, preferably 4-12; Z and z have the meaning mentioned in formula I and



where R, R₁, EO, Z, z and s have the same meaning as in formula III except that p in the group R₁ is 0, respectively.

Other preferred examples of the quaternary ammonium glycosides are compounds according to formula I where X =
 5 O(AO)_t(C_qH_{2q}) where q is 3; n = 1; r = 0 and v = 1, that are present in a mixture with quaternary ammonium compounds according to formula II where X = O(AO)_t(C_qH_{2q}) where q is 3; n = 1; r = 0; and k = 1, in a weight ratio 1:3-9:1.

Further preferred examples of quaternary ammonium
 10 glycosides are compounds according to formula I where n = 0; n₁ = 0; r = 1; y = 3; u = 1 and v = 1, that are present in a mixture with quaternary ammonium compounds according to formula II, where n = 0; n₁ = 0; r = 1; y = 3; k = 1 and l = 1, in a weight ratio 1:3-9:1.

15 Suitable examples of hydrophobic groups R in formula 1-IV are hexyl, 2-ethylhexyl, octyl, decyl, cocoalkyl, lauryl, oleyl, rapeseed alkyl and tallow alkyl.

The production of these surfactants is described in PCT/SE98/01433, where the procedure below is used.

20 The process involves the reaction between

- a) an amine compound containing at least one hydrocarbon group with 6-24 carbon atoms and at least one quaternary ammonium group, where at least one substituent is a hydroxyalkyl containing group, and
 - 25 b) a reducing saccharide or an alkyl glycoside where the alkyl group has 1-8 carbon atoms,
- at least partially in the presence of an acid.

The process described is a glycosidation or a transglycosidation reaction.

30 Quaternary ammonium glycosides III are easily produced by reacting a reducing saccharide and the quaternary ammonium compound of formula IV. Both of these starting materials are

easily available. The reaction mixtures containing essential amounts of both compound III and IV are preferably used as adjuvants without any separation of the compounds, mainly because such a separation is a costly operation. The relation
5 between quaternary ammonium glycoside surfactant and the quaternary ammonium compound could vary between 1:3 and 9:1, preferably between 2:3 and 9:1. The two other preferred groups of quaternary ammonium glycosides are also easily prepared by the same method. The quaternary ammonium
10 compounds that are used as starting materials in these cases are ethoxylated and quaternised 3-aminopropyl alkyl ethers and ethoxylated and diquaternised alkyl-1,3-diaminopropanes respectively. These compounds are also easily available, and the products resulting after the glucosidation reaction
15 function well as adjuvants for pesticides and fertilisers.

In JP 4-193891 another method for producing quaternary ammonium glycosides is described, which involves a glucosidation reaction with a polyalkyleneglycol halohydrin. The intermediate product could then be reacted with a
20 tertiary amine, yielding a quaternary product. To remove unreacted polyalkyleneglycol halohydrine, the product mixture is then purified by distillation or solvent extraction.

The quaternary ammonium glycosides could be added as adjuvants to both liquid, such as aqueous, and solid
25 agricultural compositions containing pesticides such as herbicides, acaricides, fungicides, insecticides, as well as plant growth regulators and fertilisers. Typical examples of herbicides are different amine salts of glyphosate, such as the isopropylamine salt, the dimethylamine salt and the
30 ethylenediamine salt; glufosinate, salts of 2,4-dichlorophenoxyacetic acid, salts of 4-chloro-2-methylphenoxyacetic acid, bialaphos, dicamba, diphenylethers,

imidazolinones and sulfonylureas. The preferred pesticides are the water soluble herbicides, and the most preferred herbicide is glyphosate, and the salts thereof.

Other examples of formulations where the quaternary ammonium glycosides may be used as adjuvants are
5 micronutrient solutions containing one or several micronutrients, such as iron, manganese, copper, zinc, boron and molybdenum. The micronutrients may be complexed to e.g. aminocarboxylates, such as EDTA, DTPA, HEDTA, EDDHMA and
10 EDDHA. In addition to micronutrients and chelating agents, the formulations may also contain macronutrients, such as nitrogen, phosphorus, potassium, magnesium and sulphur, and pesticides may also be included. These above-mentioned formulations are particularly suitable for foliar
15 applications.

The formulations according to the invention may also contain other additives, such as other surfactants, preservatives, additives to further enhance pesticidal activity, such as ammonium sulphate; solvents, corrosion
20 inhibitors, thickeners, sequestering agents, anti-freeze agents, anti-foam agents, anti-gelling agents and dyes.

The compositions could also contain viscosity reducing agents such as glycerol, ethylene glycol, propylene glycol and low molecular weight polyethylene or polypropylene
25 glycols.

The compositions could be concentrates as well as diluted, "ready to use", solutions. The concentrations may vary within wide limits, and a pesticide formulation could contain 0.01-99.9% by weight of a pesticide, 0-40% by weight
30 of ammonium sulphate and an amount of 0.01-70% by weight of a mixture containing quaternary ammonium glycoside surfactant and quaternary ammonium compound present in a weight ratio

1:3-9:1. As a concentrate, the concentrations are normally in the range of 4-70% for the herbicide, 2-50% for the adjuvants and 0-40% of ammonium sulphate, whereas for the ready-to-use solutions the corresponding ranges are 0.01-4%, 0.01-8% and 0-40%. The components could all be mixed in the concentrate or be tank-mixed just before spraying the solution.

A fertiliser formulation could contain 0.0001-99.9%, preferably 0.001-99.9%, by weight of a fertiliser and an amount of 0.0001-70%, preferably 0.001-70%, by weight of a mixture containing quaternary ammonium glycoside surfactant and quaternary ammonium compound present in a weight ratio 1:3-9:1. In a ready-to-use formulation the concentration of micronutrients are usually in the lower area of the range.

The following examples are illustrative of the invention and are not to be construed as a limitation of the scope.

Example 1

Biodegradability tests were performed with the "closed bottle test" as described in OECD Test 301D. 2-Ethylhexylamine that had been alkoxyated with 2 moles of propylene oxide and 4 moles of ethylene oxide, and then quaternised by methyl chloride, was compared to the glucosidised product of the same compound. After 28 days the glucosidised product had reached 43% biodegradation, whereas the unglucosidised product had only reached 11% biodegradation. Although the glucosidised product contained about 15% of unreacted quaternary ammonium compound, the biodegradation of the glucosidised product mixture was almost 4 times as fast as that of the unglucosidised product.

Example 2

The herbicidal effects of formulations containing the herbicide glyphosate and quaternary ammonium glycosides according to the present invention were investigated in

greenhouse tests. For comparison, formulations containing some of the corresponding quaternary ammonium compounds were included in the investigation.

Roundup™, which is a commercially available herbicidal standard formulation from Monsanto containing the isopropylamine salt of glyphosate and an ethoxylated fatty amine, was also included as a reference. In Roundup™ the weight ratio adjuvant/glyphosate is 1:2.

The weeds used were glasshouse grown Coachgrass (*Elymus repens*), Winter Oil Seed Rape (*Brassica napus*) and Rigid Ryegrass (*Lolium rigidum*). The treatments for *Elymus repens* and *Brassica napus* were sprayed at three dose rates; 0.15, 0.25 and 0.75 kg a.e./ha referring to glyphosate, and for *Lolium rigidum* the doses were 0.08, 0.15 and 0.25 kg a.e./ha referring to glyphosate. The recommended dose rate for glyphosate is 1.08 kg a.e./ha. There were three replicates of each treatment.

The aqueous herbicide formulations were sprayed on the plants by using a laboratory track sprayer fitted with an 80015E flat fan nozzle, at a spray pressure of 210 kPa delivering 202 litres/ha.

The following formulation recipe was used for the greenhouse tests displayed in Tables 1-6. These formulations were diluted with water before spraying.

Formulation (concentrated)

Glyphosate	13.8% w/w a.e.
Cationic adjuvant	6.9% w/w
Water	balance

To test the stability all concentrated formulations were kept at 0°C and at 54°C for two weeks. The solutions were still clear and homogenous after that time.

The diluted solutions that were sprayed had the concentrations displayed in the table below.

Dose rate (kg/ha)	Concentration of glyphosate acid equivalents (%)	Concentration of adjuvant (%)
0.75	0.37	0.18
0.25	0.12	0.06
0.15	0.07	0.04
0.08	0.04	0.02

The experiments were assessed according to the amount of green life growth and regrowth 6 weeks after spraying. A score of 0-100% was used, where 100% is a totally dead plant, and for example a 50% reduction in the amount of green growth present was scored by a comparison to the best untreated plant, the latter scoring 0%. Since the glucosidised quaternary compounds by necessity contain a lower weight content of quaternary nitrogen as compared to the corresponding quaternary ammonium compounds, an activity index was formed. The activity index is calculated by dividing the effect obtained by the number of moles of quaternary nitrogen per ha contained in the different formulations.

All products have been quaternised by methyl chloride.

Product	Moles of quaternary nitrogen per ha	Effect (%)	Activity index (effect/mole)
2-ethylhexylamine+8EO, quaternised (0.75 kg/ha)	0.705	92	130
(0.25 kg/ha)	0.235	43	183
(0.15 kg/ha)	0.141	12	85
2-ethylhexylamine+8EO, quaternised and glucosidised (0.75 kg/ha)	0.368	73	198
(0.25 kg/ha)	0.123	37	300
(0.15 kg/ha)	0.074	12	162
2-ethylhexylamine+2PO+4EO, quaternised (0.75 kg/ha)	0.794	90	113
(0.25 kg/ha)	0.265	50	189
(0.15 kg/ha)	0.159	20	126
2-ethylhexylamine+2PO+4EO, quaternised and glucosidised (0.75 kg/ha)	0.391	97	248
(0.25 kg/ha)	0.130	47	361
(0.15 kg/ha)	0.078	13	167
n-octylamine+8EO, quaternised (0.75 kg/ha)	0.705	95	135
(0.25 kg/ha)	0.235	45	191
(0.15 kg/ha)	0.141	8	57
n-octylamine+8EO, quaternised and glucosidised (0.75 kg/ha)	0.368	93	253

(0.25 kg/ha)	0.123	35	285
(0.15 kg/ha)	0.074	12	162
n-octylamine+2PO+4EO, quaternised (0.75 kg/ha)	0.794	85	107
(0.25 kg/ha)	0.265	47	177
(0.15 kg/ha)	0.159	5	31
n-octylamine+2PO+4EO, quaternised and glucosidised (0.75 kg/ha)	0.391	95	242
(0.25 kg/ha)	0.130	50	385
(0.15 kg/ha)	0.078	17	218

Table 1. Greenhouse test with *Brassica napus*. The dose rates are referring to the amount of glyphosate, the amount of cationic adjuvant being half of that amount.

Product	Moles of quaternary nitrogen per ha	Effect (%)	Activity index (effect/mole)
2-ethylhexylamine+8EO, quaternised (0.25 kg/ha)	0.235	95	404
(0.15 kg/ha)	0.141	65	461
(0.08 kg/ha)	0.075	33	440
2-ethylhexylamine+8EO, quaternised and glucosidised (0.25 kg/ha)	0.123	85	691
(0.15 kg/ha)	0.074	68	919
(0.08 kg/ha)	0.039	28	718
2-ethylhexylamine+2PO+4EO, quaternised (0.25 kg/ha)	0.265	90	340

(0.15 kg/ha)	0.159	67	421
(0.08 kg/ha)	0.085	27	318
2-ethylhexylamine+2PO+4EO, quaternised and glucosidised (0.25 kg/ha)	0.130	90	692
(0.15 kg/ha)	0.078	50	641
(0.08 kg/ha)	0.042	48	1143
n-octylamine+8EO, quaternised (0.25 kg/ha)	0.235	92	391
(0.15 kg/ha)	0.141	72	511
(0.08 kg/ha)	0.075	40	533
n-octylamine+8EO, quaternised and glucosidised (0.25 kg/ha)	0.123	93	756
(0.15 kg/ha)	0.074	53	716
(0.08 kg/ha)	0.039	17	436
n-octylamine+2PO+4EO, quaternised (0.25 kg/ha)	0.265	97	366
(0.15 kg/ha)	0.159	60	377
(0.08 kg/ha)	0.085	40	471
n-octylamine+2PO+4EO, quaternised and glucosidised (0.25 kg/ha)	0.130	92	708
(0.15 kg/ha)	0.078	62	795
(0.08 kg/ha)	0.042	33	785

Table 2. Greenhouse test with *Lolium rigidum*. The dose rates are referring to the amount of glyphosate, the amount of cationic adjuvant being half of that amount.

Product	Moles of quaternary nitrogen per ha	Effect (%)	Activity index (effect/mole)
2-ethylhexylamine+8EO, quaternised (0.75 kg/ha)	0.705	93	132
(0.25 kg/ha)	0.235	73	311
(0.15 kg/ha)	0.141	60	426
2-ethylhexylamine+8EO, quaternised and glucosidised (0.75 kg/ha)	0.368	97	264
(0.25 kg/ha)	0.123	67	545
(0.15 kg/ha)	0.074	47	635
2-ethylhexylamine+2PO+4EO, quaternised (0.75 kg/ha)	0.794	95	120
(0.25 kg/ha)	0.265	65	245
(0.15 kg/ha)	0.159	37	233
2-ethylhexylamine+2PO+4EO, quaternised and glucosidised (0.75 kg/ha)	0.391	92	235
(0.25 kg/ha)	0.130	65	500
(0.15 kg/ha)	0.078	45	576
n-octylamine+8EO, quaternised (0.75 kg/ha)	0.705	97	138
(0.25 kg/ha)	0.235	73	311
(0.15 kg/ha)	0.141	53	376
n-octylamine+8EO, quaternised and glucosidised (0.75 kg/ha)	0.368	92	250

(0.25 kg/ha)	0.123	75	610
(0.15 kg/ha)	0.074	62	838
n-octylamine+2PO+4EO, quaternised (0.75 kg/ha)	0.794	93	117
(0.25 kg/ha)	0.265	68	257
(0.15 kg/ha)	0.159	52	327
n-octylamine+2PO+4EO, quaternised and glucosidised (0.75 kg/ha)	0.391	97	248
(0.25 kg/ha)	0.130	72	554
(0.15 kg/ha)	0.078	63	808

Table 3. Greenhouse test with *Elymus repens*. The dose rates are referring to the amount of glyphosate, the amount of cationic adjuvant being half of that amount.

Product	Effect (%)
3-aminopropyl C ₈ -C ₁₀ -alkyl ether+5EO, quaternised and glucosidised (0.75 kg/ha)	97
(0.25 kg/ha)	45
(0.15 kg/ha)	10
N-tallow-1,3-propylenediamine+12EO, quaternised and glucosidised (0.75 kg/ha)	100
(0.25 kg/ha)	48
(0.15 kg/ha)	18
Roundup TM (0.75 kg/ha)	100
(0.25 kg/ha)	33
(0.15 kg/ha)	25

5 Table 4. Greenhouse test with *Brassica napus*. The dose rates are referring to the amount of glyphosate, the amount of cationic adjuvant being half of that amount.

Product	Effect (%)
3-aminopropyl C ₈ -C ₁₀ -alkyl ether+5EO, quaternised and glucosidised (0.25 kg/ha)	92
(0.15 kg/ha)	92
(0.08 kg/ha)	72
N-tallow-1,3-propylenediamine+12EO, quaternised and glucosidised (0.25 kg/ha)	100
(0.15 kg/ha)	95
(0.08 kg/ha)	57
Roundup™ (0.25 kg/ha)	98
(0.15 kg/ha)	93
(0.08 kg/ha)	22

Table 5. Greenhouse test with *Lolium rigidum*. The dose rates are referring to the amount of glyphosate, the amount of cationic adjuvant being half of that amount.

Product	Effect (%)
3-aminopropyl C ₈ -C ₁₀ -alkyl ether+5EO, quaternised and glucosidised (0.75 kg/ha)	93
(0.25 kg/ha)	75
(0.15 kg/ha)	62
N-tallow-1,3-propylenediamine+12EO, quaternised and glucosidised (0.75 kg/ha)	93
(0.25 kg/ha)	70
(0.15 kg/ha)	52
Roundup™ (0.75 kg/ha)	93
(0.25 kg/ha)	65
(0.15 kg/ha)	42

5 **Table 6.** Greenhouse test with *Elymus repens*. The dose rates are referring to the amount of glyphosate, the amount of cationic adjuvant being half of that amount.

As is shown from the tables, the quaternary ammonium glucosides according to the present invention are more efficient adjuvants for the herbicide than the corresponding unglucosidised quaternary ammonium compounds that are used as starting materials for the glucosides, when the compounds are compared on a molar basis. The formulations based on the quaternary ammonium glucosides also exhibit comparable or better herbicidal efficacy than the Roundup formulation.

Example 3

Some of the quaternary ammonium glucosides according to the present invention were also investigated as adjuvants in the presence of ammonium sulphate. These formulations were compared to the corresponding formulations containing no ammonium sulphate.

RoundupTM was used as a reference. In RoundupTM the ratio adjuvant/glyphosate is 1:2. It is not possible to add ammonium sulphate to RoundupTM, because that makes the product to turn into a gel.

The weeds used were glasshouse grown Coachgrass (*Elymus repens*), Winter Oil Seed Rape (*Brassica napus*) and Rigid Ryegrass (*Lolium rigidum*). The treatments were sprayed at the dose rates 0.25 (for *Lolium rigidum* and *Elymus repens*) and 0.75 kg a.e./ha (for *Brassica napus*); the dose rates referring to glyphosate. There were three replicates of each treatment.

Formulations with ammonium sulphate

Formulation A

Glyphosate	13.8% w/w a.e.
Cationic adjuvant	13.8% w/w
Ammonium sulphate	15% w/w
Water	balance

Formulation B

	Glyphosate	13.8% w/w a.e.
	Cationic adjuvant	6.9% w/w
	Ammonium sulphate	15% w/w
5	Water	balance

Formulations without ammonium sulphate**Formulation C**

	Glyphosate	13.8% w/w a.e.
	Cationic adjuvant	13.8% w/w
10	Water	balance

Formulation D

	Glyphosate	13.8% w/w a.e.
	Cationic adjuvant	6.9% w/w
15	Water	balance

The stability of the formulations was tested by keeping them for two weeks at 0 and 54°C. All the solutions were still clear and homogeneous after that time. The diluted solutions that were sprayed had the concentrations displayed in the table below.

Formu- lation	Dose rate (kg/ha)	Conc. of Glyphosate acid equiv. (%)	Conc. Of ammonium sulphate (%)	Conc. of adjuvant (%)
A	0.75	0.37	0.40	0.37
B	0.75	0.37	0.40	0.18
C	0.75	0.37	0	0.37
D	0.75	0.37	0	0.18
A	0.25	0.12	0.13	0.12
B	0.25	0.12	0.13	0.06
C	0.25	0.12	0	0.12
D	0.25	0.12	0	0.06

The experiments were assessed for the amount of green live growth and regrowth 6 weeks after spraying for *Brassica napus* and *Lolium rigidum* and 8 weeks after spraying for *Elymus repens*. A score of 1-10 was used, where 0 = dead, 5 = 50% reduction in the amount of green growth present in comparison with the best untreated and 10 = as best untreated.

Product	Effect (score 0-10)
Cocoamine+4EO, quaternised and glucosidised.	
Formulation C (no ammonium sulphate)	1.7
Formulation A (with ammonium sulphate)	0.0
Cocoamine+6EO, quaternised and glucosidised.	
Formulation C (no ammonium sulphate)	2.7
Formulation A (with ammonium sulphate)	0.0
Cocoamine+4EO, quaternised and glucosidised.	
Formulation D (no ammonium sulphate)	2.3
Formulation B (with ammonium sulphate)	0.0
Cocoamine+6EO, quaternised and glucosidised.	
Formulation D (no ammonium sulphate)	3.0
Formulation B (with ammonium sulphate)	2.0
Roundup TM	1.2

Table 7. Greenhouse test with *Brassica napus*. The dose rate is 0.75 kg a.e./ha, referring to the amount of glyphosate.

Product	Effect (score 0-10)
Cocoamine+4EO, quaternised and glucosidised. Formulation C (no ammonium sulphate)	0.0
Formulation A (with ammonium sulphate)	0.0
Cocoamine+6EO, quaternised and glucosidised. Formulation C (no ammonium sulphate)	0.0
Formulation A (with ammonium sulphate)	0.0
Cocoamine+4EO, quaternised and glucosidised. Formulation D (no ammonium sulphate)	1.0
Formulation B	0.0
Cocoamine+6EO, quaternised and glucosidised, Formulation D (no ammonium sulphate)	0.3
Formulation B	0.0
Roundup TM	0.3

Table 8. Greenhouse test with *Lolium rigidum*. The dose rate is 0.25 kg a.e./ha, referring to the amount of glyphosate.

Product	Effect (score 0-10)
Cocoamine+4EO, quaternised and glucosidised, Formulation C (no ammonium sulphate)	0.0
Formulation A (with ammonium sulphate)	0.0
Cocoamine+6EO, quaternised and glucosidised. Formulation C (no ammonium sulphate)	0.7

Formulation A (with ammonium sulphate)	0.3
Cocoamine+4EO, quaternised and glucosidised.	
Formulation D (no ammonium sulphate)	1.3
Formulation B (with ammonium sulphate)	0.3
Cocoamine+6EO, quaternised and glucosidised.	
Formulation D (no ammonium sulphate)	0.7
Formulation B (with ammonium sulphate)	0.3
Roundup™	0.3

Table 9. Greenhouse test with *Elymus repens*. The dose rate is 0.25 kg a.e./ha, referring to the amount of glyphosate.

5 The examples show that the addition of ammonium sulphate further enhances the herbicidal activity of the formulations. The best results were obtained with formulations containing ammonium sulphate and where the weight ratio between adjuvant and glyphosate was 1:1.

Example 4

10 Foam height measurements were performed according to the standard Ross Miles procedure. The foam height was measured immediately and after 5 minutes. The test was made at 50°C using 0.05% (w/w) surfactant solutions. The glucosidised products are compared to the corresponding unglucosidised
15 quaternary ammonium compounds. The adjuvant used in Roundup™ is also included as a reference.

Product	Foam height (mm) after 0 min	Foam height (mm) after 5 min
2-ethylhexylamine+8EO, quaternised	15	0
2-ethylhexylamine+8EO, quaternised and glucosidised	13	0
2-ethylhexylamine+2PO+4EO, quaternised	6	0
2-ethylhexylamine+2PO+4EO, quaternised and glucosidised	3 ¹	0
n-octylamine+8EO, quaternised	45	4
n-octylamine+8EO, quaternised and glucosidised	35	3
n-octylamine+2PO+4EO, quaternised	7	0
n-octylamine+2PO+4EO, quaternised and glucosidised	8 ¹	0
Tallowamine ethoxylate (adjuvant in Roundup™)	95	5

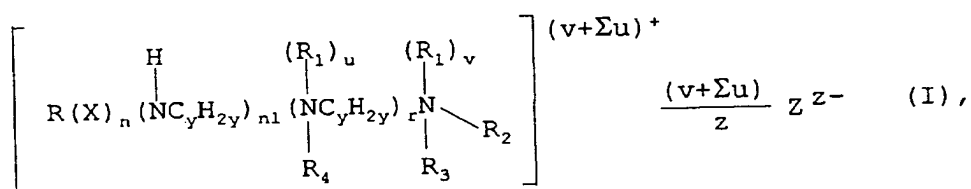
Table 10. Foam height measurements.

¹The foam collapses after 3 s

5 The quaternary ammonium glucosides are more low-foaming than the corresponding quaternary ammonium compounds, and much more low-foaming than the adjuvant used in Roundup™. The foam that the glucosides generate collapses quickly, in some instances almost instantaneously.

C L A I M S

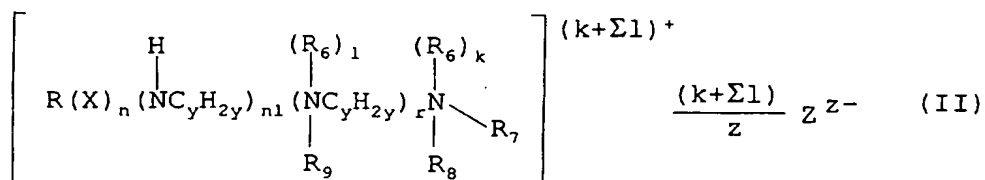
1. Use of a quaternary ammonium glycoside surfactant containing at least one hydrocarbon group with 6-24 carbon atoms and at least one quaternary ammonium group where at least one substituent is an alkyleneoxy containing group which is connected to a saccharide residue by a glycosidic bond, as an adjuvant for pesticides and fertilisers.
2. Use of a quaternary ammonium glycoside surfactant according to claim 1, where the substituent has the formula $(AO)_s(G)_p$, where AO is an alkyleneoxy group with 2-4 carbon atoms, G is a saccharide residue, p is a number from 1 to 10 and s is a number from 1-15.
3. Use according to claim 1 or 2 of a quaternary ammonium glycoside surfactant, where the surfactant has the formula



where R is an aliphatic group with 6-24 carbon atoms; R_1 is an aliphatic group with 1-4 carbon atoms or $(AO)_s(G)_p$; R_2 , R_3 and R_4 independently are a group $(AO)_s(G)_p$, an aliphatic group with 1-24 carbon atoms or a hydroxyalkyl group with 2-4 carbon atoms; AO is an alkyleneoxy group with 2-4 carbon atoms; s is 0-15 and $\Sigma s = 1-30$; G is a saccharide residue which is connected to the rest of the molecule by a glycosidic bond and p (the degree of polymerisation) is 0-10; $\Sigma p = 1-20$; $r = 0-3$; $y = 2-3$; $X = \text{CO}$ or $\text{COO(AO)}_t(\text{C}_q\text{H}_{2q})$ or $\text{O(AO)}_t(\text{C}_q\text{H}_{2q})$; $n = 0$ or 1; n_1 is 0 except when X is CO, then n_1

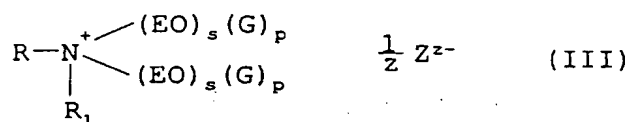
is 1; $q = 2-4$; $t = 0-4$; $u = 0$ or 1 and $v = 0$ or 1 , provided that the sum $(v + \sum u)$ is $1-3$; Z is an anion and z is the charge of the anion Z .

4. Use according to claim 3, where the quaternary ammonium glycoside surfactant is present in a mixture with a
5 quaternary ammonium compound having the formula



- 10 where R_6 is independently an aliphatic group with 1-4 carbon atoms or $-\text{CH}_2\text{CH}_2\text{OH}$; R_7 , R_8 , and R_9 independently are a group
15 $(\text{AO})_s$, an aliphatic group with 1-24 carbon atoms or a hydroxyalkyl group with 2-4 carbon atoms; $l = 0$ or 1 and $k = 0$ or 1 , provided that the sum $(k + \sum l)$ is $1-3$; and R , AO , s , X , n , n_1 , y and r have the same meaning as in claim 3, in a weight ratio $1:3-9:1$.

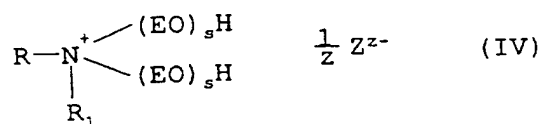
5. Use according to claim 3, where the quaternary ammonium glycoside surfactant has the formula



where R is an aliphatic group with 6-24 carbon atoms; R_1 is an aliphatic group with 1-4 carbon atoms or the group $\text{C}_2\text{H}_4\text{O}(\text{G})_p$; G is a saccharide residue that is connected to the

polyethyleneoxy chain by a glycosidic bond and p (the degree of polymerisation) is 0-10; Σp is 1-15; EO is an ethyleneoxy group; s is 0-12; Σs is 2-15; Z and z have the meaning mentioned in formula I in claim 3.

- 5 6. Use according to claim 5, where the quaternary ammonium glycoside surfactant is present in a mixture with a quaternary ammonium compound having the formula



- 10 where R, R₁, EO, Z, z and s, have the same meaning as in formula III in claim 5, except that p in the group R₁ is 0, in a weight ratio 1:3-9:1.

7. Use according to claim 3, where $\text{X} = \text{O}(\text{AO})_t(\text{C}_q\text{H}_{2q})$ where q is 3; n = 1; r = 0 and v = 1.

- 15 8. Use according to claim 7 where the quaternary ammonium glycoside is present in a mixture with a quaternary ammonium compound according to claim 4, where $\text{X} = \text{O}(\text{AO})_t(\text{C}_q\text{H}_{2q})$ where q is 3; n = 1; r = 0; and k = 1, in a weight ratio 1:3-9:1.

9. Use according to claim 3, where n = 0; n₁ = 0; r = 1; y = 3; u = 1 and v = 1.

- 20 10. Use according to claim 9, where the quaternary ammonium glycoside is present in a mixture with a quaternary ammonium compound according to claim 4, where n = 0; n₁ = 0; r = 1; y = 3; k = 1 and l = 1, in a weight ratio 1:3-9:1.

- 25 11. Use according to any of the preceding claims 1-10 where the quaternary ammonium glycoside surfactant and the mixture thereof is used as an adjuvant for a herbicide.

12. Use according to claim 11, where the herbicide is glyphosate.

13. A pesticide formulation, characterised in that it contains 0.01-99.9% by weight of a pesticide, 0-40% by weight of ammonium sulphate and an amount of 0.01-70% by weight of a mixture in accordance with claim 4, 6, 8 or 10.

5 14. A liquid formulation according to claim 9, characterised in that the pesticide is glyphosate, which is present in an amount of 0.02-70% by weight.

15. Use according to any of the preceding claims 1-10 where the quaternary ammonium glycoside surfactant and the mixture thereof is used as an adjuvant for a fertiliser.

10 16. A fertiliser formulation characterised in that it contains 0.0001-99.9% by weight of a fertiliser and an amount of 0.0001-70% by weight of a mixture in accordance with claim 4, 6, 8 or 10.

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A B S T R A C T

The present invention relates to the use of a quaternary ammonium glycoside surfactant as an adjuvant for fertilisers or pesticides, such as herbicides. The surfactant contains at least one hydrocarbon group with 6-24 carbon atoms and at least one quaternary ammonium group where at least one substituent is an alkyleneoxy containing group which is connected to a saccharide residue by a glycosidic bond. Also compositions containing pesticides or fertilisers are described.

These quaternary ammonium glycoside surfactants have, in comparison with prior known quaternary ammonium surfactants that have been used as adjuvants, an essentially improved biodegradability. They also improve the uptake and efficacy of fertilisers and herbicides.